

(12) **UK Patent Application** (19) **GB** (11)

**2 147 614 A** ✓

(43) Application published 15 May 1985

(21) Application No 8326344

(22) Date of filing 1 Oct 1983

(71) Applicant  
Kenneth Porter,  
7 North Park Road, Harrogate, North Yorkshire HG1 5PD

(72) Inventor  
Kenneth Porter

(74) Agent and/or Address for Service  
Kenneth Porter, 7 North Park Road, Harrogate, North  
Yorkshire HG1 5PD

(51) INT CL<sup>4</sup>  
D06P 5/20

(52) Domestic classification  
D1B 2C1B4

(56) Documents cited  
None

(58) Field of search  
D1B

**(54) Heat transfer printing**

(57) The invention provides a structureless medium which is 'transparent' to sublimable dye during the heat transfer printing process. The structureless, dye-transparent medium may be employed in two ways. It may be used to carry a design which is impermeable to sublimable dye so that a reserved print of the decorative design may be obtained on a suitable dye-receptive substrate of thermoplastic fabric or film by interposing the medium plus the impermeable decorative design between a sheet of heat transfer material and the substrate during heat transfer printing. Since the plastic film medium plus the impermeable decorative design (which are preferably adhesively combined) are not damaged during the heat transfer printing process, they may be re-used any number of times to impose the same design on further samples of the substrate using new transfer material at each printing. Alternatively, the structureless, dye-transparent medium may be interposed between a sheet of heat transfer material and a dye-receptive substrate when it is desired to avoid contamination of the substrate by materials other than the sublimable dye (such as adhesives, resins, binders, etc) which may be present on the sheet of transfer material.

GB 2 147 614 A

2147614

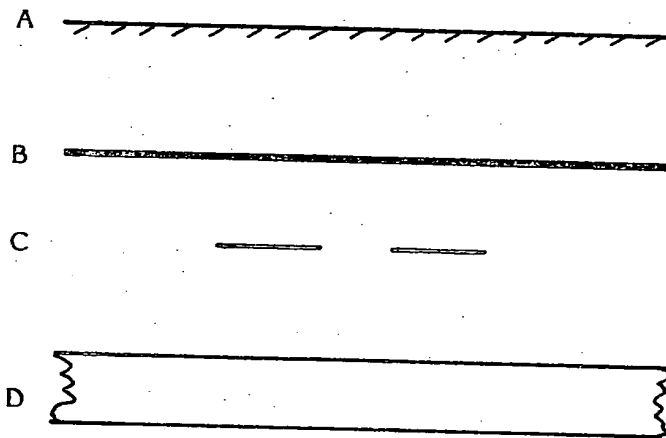


Figure 1

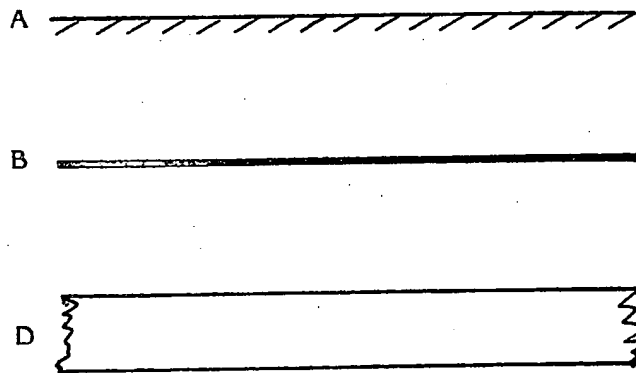


Figure 2

2147614

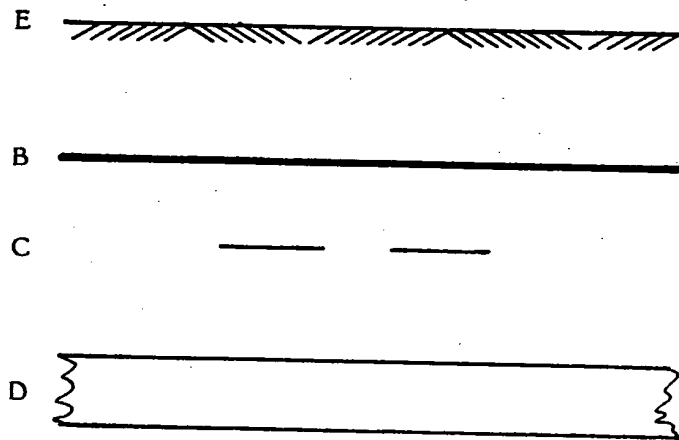


Figure 3

## SPECIFICATION

### Heat transfer printing

5 This invention relates to heat transfer printing using sublimable dyes. The invention provides a structureless medium which is 'transparent' to sublimable dye during the heat transfer process. The structureless, dye-transparent medium may be employed in two  
10 ways. It may be used to carry a design which is impermeable to sublimable dye so that a reserved print of the decorative design can be obtained on a suitable dye-receptive substrate of thermoplastic fabric or film by interposing the medium plus the  
15 impermeable decorative design between a sheet of heat transfer material and the substrate during heat transfer printing. Alternatively, the structureless, dye-transparent medium may be interposed between a sheet of heat transfer material and a dye-receptive  
20 substrate when it is desired to avoid contamination of the substrate by materials other than the sublimable dye (such as adhesives, resins, etc) which may be present on the sheet of transfer material.

It is already known to produce decorated fabrics and  
25 plastics by exposing them to a sheet of transfer material, such as a smooth sheet of paper carrying a vapourisable or sublimable dyestuff. By the application of heat to the transfer sheet when pressed against the fabric or plastic, the dyestuff is caused to migrate  
30 to the fabric or plastic in vapour form and there is produced on the fabric or plastic a reverse replica of the decorative design in which the dyestuff was laid down on the transfer sheet. During this heat transfer process, a substantial proportion of the dyestuff  
35 carried on the transfer sheet is removed by the migration process and the decorative design may thus only be printed once on the substrate at its full required strength. This is not a disadvantage if many thousands of articles of fabric or plastic are required to  
40 be decorated because the costs of preparing the artwork for the decorative design and the costs of preparing the sheets of transfer material on expensive equipment are amortised over many thousands of identical sheets of transfer material. If only one of two  
45 articles of fabric or plastic are to be decorated, then this also is inexpensive as the sheets of transfer material may be prepared by a number of means, for example, by the assembly of non-transferably marked sub-units of the decorative design as in my copending  
50 Application Number 8,323,668 or by hand drawing or painting with special caryons, paints or felt-tipped markers containing sublimable dyes or by the use of an electrophotographic process as described in British Patent Specification 1,497,457. Unfortunately, however,  
55 in the case of assembling non-transferably marked sub-units or hand drawing or painting, it is expensive and time-consuming to prepare more than a small number of identical designs. In fact, with hand drawing or painting it is virtually impossible to  
60 prepare even two identical designs because of variations that arise naturally in the depth of colour laid down each time by the artist or by slight variations in the width and placing of brush or caryon lines. In the case of the electrophotographically prepared sheets  
65 of transfer material, although this process is suitable

for preparing between, say, two and a hundred sheets of transfer material from one piece of artwork, unfortunately the cost of the equipment is high (leading to a high cost per sheet of transfer material) and the quality of the final transferred design is not satisfactory for critical applications. In particular, the electrophotographic process cannot be set up so that there is a complete absence of sublimable dye in the areas of the sheet of transfer material where no  
70 decoration is intended to be present. There is always present a small amount of sublimable dye in the form of speckles in what should be clear areas of the sheet of transfer material (especially near the edges of any part of the decorative design) and during the heat transfer  
75 process these speckles of dye produce coloured or black speckles (according to the dye colour) in the background of the decorative design on the substrate. These speckles are aesthetically unattractive and whilst they may sometimes be scraped off the sheet of transfer material before it is heated in contact with the  
80 substrate, this cannot be done with complicated or intricate decorative designs because of the danger of damaging wanted parts of the sheet of transfer material. It is also known in the art of heat transfer  
85 printing to decorate suitable substrates by heat transfer printing through a porous material which may or may not have an affinity for the sublimable dye and which may or may not be permeable to the dye vapour. Such processes are referred to in United  
90 States Patent 4,049,374. In this publication an embossing sheet having no affinity or retention property for sublimable dyes is interposed between the transfer sheet and the substrate during the application of heat and pressure. This embossing sheet is made of a  
95 porous material such as fibreglass which can let through the major part of the subliming dyestuff as vapour. With this process there is obtained on the fabric or plastic an embossing or surface texturing effect practically without any change in the design  
100 transferred to the fabric or plastic. However, there is some change in the the design because the embossing sheet is not uniformly permeable to the vapour of the sublimable dyestuff and, in addition, by its textured nature, the embossing sheet cannot be in  
105 such intimate contact with the substrate that some of the dye vapour cannot be prevented from 'wandering' in the interstices of the embossing sheet and thereby blurring the definition of fine lines or colour boundaries forming part of the decorative design. Another  
110 process (also referred to in United States Patent 4,049,374) employing an embossing sheet is one in which the embossing sheet is substantially or largely impermeable to the dyestuff vapour or has an affinity for the dyestuff so that the dyestuff reaches the fabric  
115 or plastic only through defined perforations in the embossing sheet to define the embossing pattern therein and hence colours only the portions of the fabric or plastic opposite the perforations. In this process, the dyestuff appears on the fabric or plastic in a pattern which is a subtractive combination of the  
120 pattern which is present on the transfer sheet with the perforation pattern on the embossing sheet. Usually the embossing sheet (for example, a lace, crochet work or other openwork type of fabric) is soiled with  
125 the dyestuff during the transfer operation and can be  
130

used once only, unless a cleaning operation is performed on it; of course, the fabric or plastic is also embossed with the pattern of the embossing sheet.

I have now found a way of transfer printing designs on to fabrics and plastics in which a design which is reserved in some suitable impermeable substance is supported on a plastic film which is permeable at the molecular level to sublimable dyestuffs whereby such a combination may be used time after time to transfer the design to the fabric or plastic without embossing the fabric or plastic during the transfer printing process, without any hint of the structure of the supporting film appearing in the transferred design and without any need for cleaning the plastic film, unlike the effects observed with previous permeable embossing sheets. I have also found that this invention may be used in the transfer of designs to fabrics and plastics where it is desirable or essential that materials such as adhesives, resins, carriers, etc present on the sheet of transfer material carrying the design in sublimable dyestuff do not contaminate the fabric or plastic.

According to the present invention there is provided a means of heat transfer printing in which sublimable dye is transferred to a receiving substrate by molecular diffusion through a removable plastic film having an affinity for the sublimable dye.

Thus, in particular, the decorations which it is desired to transfer print upon substrates of fabric or plastic may be any of an almost infinite range of designs. For example, they may be names or slogans together with photographs, sketches or caricatures of artists, singers, politicians or other well known figures. They may be geometrical or abstract designs. Such designs may be required to be imposed upon T-shirts, sweaters, caps, blouses, dresses or other garments or textiles. It may be desired to impose the design in more than one place on the article in which case it may be essential that the designs in all places are identical. Designs may be in a single colour or in multiple colours. Other possibilities are decorative or descriptive labels in shops or stores or transparent or opaque panels for use in displays and exhibitions or murals or decorative surfaces in or on buildings or vehicles, etc. Many possibilities suggest themselves once the basic invention is disclosed. Since the decoration is only transferred to the substrate of fabric or plastic when the article is required, the heat transfer printing process eliminates the costly holding of stocks of ready printed articles. However, with the conventional transfer printing process, it is still necessary to hold stocks of sheets of transfer material on which the designs are already carried. However, with the process of the present invention (when it is employed for carrying impermeable decorative designs), the number of designs of sheets of transfer material required to be held in stock is very much reduced because the decorations are partially or wholly generated from the impermeable designs carried on the structureless, dye-transparent medium.

The heat transfer process will work satisfactorily with a number of materials which are, generally speaking, thermoplastics. Thus the substrates to be decorated may be composed of a textile material, a nonwoven article, paper or any surface (such as metal,

plastic, wood, etc) impregnated, coated or covered with or consisting of an acrylic polymer, polyamide, polyester, epoxy resin, vinyl resin or polyurethane.

Preferred substrates are textiles containing 50% or more of surface fibres of polyester or polyamide or a sheet of plastic material or plastic coated material where the plastic is a linear or cross-linked polyester or polyamide. Polyethylene terephthalate or nylon 6:6 sheet with oriented molecules, optionally containing a white or coloured pigment are materials even more to be preferred. Such plastic sheets may be adhered to a support of paper, plastic, metal, etc or they may be coated with a thin metallic film or other coating on the opposite face to that which is to be decorated. The heat transfer process is advantageously carried out by heating the sheet of transfer material in contact with the substrate of fabric or plastic at a temperature above 140°C and preferably above 170°C. Obviously the preference for this temperature imposes limits on the thermoplastics which may be employed since they must be chemically and physically stable at the transfer temperature. The heating operation is preferably carried out for between 10 and 60 seconds and more preferably between 15 and 45 seconds.

Transfer sheets are normally prepared by conventional processes used for printing or forming designs on paper or similar surfaces, for example, by hand drawing or painting, by printing by any of the known means such as flexography, gravure, letter press, screen printing, lithography, etc or by any other means which leads to a sharp and distinct image free from speckle or other extraneous transferable item. Many materials such as paper or metal foil such as aluminium foil may be used for the transfer sheets. For the sake of good receptivity to the ink, low cost and ease of supply, paper is preferred and a lightweight, chemically pure grade manufactured especially as a transfer printing article is a suitable product since many ranges of suitable inks are available for use with and are especially compatible with such papers. The decorative design may be printed as it is required to appear on the substrate of fabric or plastic or it may need to be printed as a mirror image of its final appearance. If the decorative design is to be viewed through the substrate (ie if the substrate is transparent plastic film or sheet) then the decorative design does not require to be present as a mirror image. If, however, the decorative design is to be viewed on the surface of the article, then it must be in mirror image form. Inks containing vapourisable dyes are readily available in ranges suitable for application by any of the techniques mentioned above for the imposition of the decorative design on the transfer sheet. It is desirable when preparing multicolour transfer sheets to use a range of inks supplied by one manufacturer because in such a range, the vapourisable dyes will have been chosen to be especially compatible, that is to say, they will transfer to a similar extent when subjected to similar time and temperature treatments in the heat transfer printing process. In general, heat transfer dyes are classified as high, medium or low energy according to the time and temperature conditions which are required to cause them to transfer. It is believed that, during the transfer process, the dyes vapourise and reach the surface of the substrate to

which they are to be transferred (and which must have an affinity for the dyes) and thus the energy classification is to some extent related to the vapour pressure at the transfer temperature. Possible mechanisms for the process of simultaneously embossing and transfer printing as described in United States Patent 4,049,374 may be proposed, based on the above theory of transfer printing. In the case of the invention claimed in Claim 1 of United States Patent 4,049,374 an embossing sheet is used which has no affinity for the sublimable dyes but which is permeable to the vapour of such dyes during the heat transfer process. Typically, the embossing sheet may be spun-laced rayon nonwoven fabric. This embossing sheet is permeable to the dye vapour not only due to the material of which it is made but also to its construction which is sufficiently loose and porous to permit the ready passage of dye vapour between the filaments of the sheet. In United States Patent 4,049,374 is also mentioned a different process for simultaneously embossing and transfer printing in which the material of the embossing sheet is either substantially or largely impermeable to the dyestuff or has an affinity for it so that the vapour of the dyestuff reaches the substrate only through defined perforations in the embossing sheet and hence colours the substrate only in the pattern defined by these holes. In this case, the embossing sheet interferes in a defined manner with the passage of dye vapour from the sheet of transfer material to the substrate. Lastly, there is claimed in Claim 2 of United States Patent 4,049,374 the use of a vapour permeable embossing sheet into which is incorporated a dye trap in a defined pattern. The dye trap absorbs the dye vapour and so appears as a further pattern superimposed on the pattern in which the dye is present on the sheet of transfer material. It is not stated in United States Patent 4,049,374 whether the embossing sheet with the dye trap may be used more than once without cleaning the dye off the material used as the dye trap but it is readily apparent to anyone skilled in the art that the material of the dye trap (which may be an acrylic resin) will be soiled by the dye during its trapping action and that it can only be used once as is the case with the embossing sheets described in United States Patent 4,049,374 which have an affinity for the dyestuff.

In the process of the present invention, a removable plastic film is interposed between the sheet of transfer material and the substrate. The plastic film may be used either to carry a design in material impermeable to vapourisable dye, and so to form a reserved pattern on the substrate, or it may be used to prevent contamination of the surface of the substrate by materials present on the sheet of transfer material. The mode of action of this invention is quite different to that described in United States Patent 4,049,374 because the plastic film is not porous as are the embossing sheets described in the above United States patent. It is apparent that a simple test would easily illustrate this fact. For example, water containing a small amount of wetting agent (such as a domestic washing up liquid) would easily flow through the embossing sheets described in the above United States patent whereas it would not pass at all through the plastic film of the present invention.

Secondly, the plastic film of the present invention has an affinity for the sublimable dye and yet it does not require cleaning after each transfer process. Since the plastic film has an affinity for the sublimable dye, it is coloured by the dye and clearly a new piece of film will be required each time the decorative design is changed. However, virtually any number of transfer prints may be made of any particular decorative design using a single piece of film. This is possible because the sublimable dye (which reaches the surface of the plastic film by vapour transfer) passes through the plastic film by molecular diffusion and will then form vapour which passes to the surface of the substrate by vapour transfer. That this is the case is illustrated by the fact that the first two or three transfer prints made using a relatively thick plastic film are not at full depth of colour. It is only when the dye concentration has built up through the thickness of the plastic film that full depth prints are obtained on the substrate. Of course, to maintain the concentration of dye in the plastic film it is necessary that a new transfer sheet is used each time a print is made on the substrate. In this way, a suitable dye concentration gradient is established in the plastic film. Since the dye concentration gradient is established more rapidly in thinner films, it is preferred to use the thinnest plastic film possible. However, the thinnest plastic films are very delicate and the cost per unit area increases as the thickness is reduced because of the increased difficulty of manufacture. This invention will work with films of virtually any thickness but in order to establish the dye concentration gradient rapidly (that is, after only a few transfers) it is preferable that the plastic film is less than 50 $\mu$  thick. For ease of handling, it is also preferred that the plastic film is more than 2 $\mu$  thick. Even more to be preferred are plastic films between 2 $\mu$  and 10 $\mu$  thick since these give a good balance of cost and technical properties. In the case where the plastic film of the invention is used to protect the surface of a substrate from contamination during heat transfer printing, it is preferable that it is as thin as possible and films at the lower end of the 2 $\mu$  to 10 $\mu$  range are recommended. In order to save handling the unsupported plastic film, it may be releasably adhered to the surface of the substrate, especially where the substrate is a plastic sheet. After the heat transfer printing process has been completed, the plastic film may then be peeled off the substrate and disposed of, together with any contaminating materials.

The process of this invention when used for preparing multiple transfer prints by supporting an impermeable design on the plastic film is ideally suited to the preparation of single colour designs. In this case, the sheet of transfer material is uniformly coated with a layer of sublimable dye (preferably contained in an ink medium and deposited on the transfer sheet by one of the printing processes mentioned above). Multicolour designs may be heat transfer printed by the process of this invention using multicolour transfer sheets but it is essential that the design on the multicolour transfer sheets be registered exactly with the design which becomes imprinted on the plastic film. Of course, this is simpler in the case where the multicolour design consists of, say, a few blocks of solid colour than where the

multicolour design consists of, say, a four-colour half-tone design. It is also desirable when using the process of this invention to print multiple, multicolour designs, to use the thinnest possible plastic film since this limits the amount of 'spreading' of any colour boundaries by sideways diffusion of the dye in the plastic film. When the process of this invention is used for contamination prevention, no registration of multicolour designs is necessary, of course, because each plastic film is used only once.

The composition and properties of the plastic film used in this invention are quite important. It is necessary, as has been stated, for the plastic film to possess some affinity for the sublimable dyes to be used. This may be used as one of the criteria for the selection of the plastic film since during carrying out the process of this invention, the plastic film will become coloured by the dyestuffs used. However, unlike the substrate, the fastness properties of the dyed plastic film are unimportant and if a very low rub fastness is apparent, for example, then this does not matter because at the end of the operation, the plastic film will be discarded or stored in some suitable container for later re-use. A very low rub fastness for the dyed plastic film most likely indicates that whilst the dye molecules can diffuse freely within the film, the affinity of the molecules of the dye for those of the plastic is relatively weak. It is essential that the plastic film is continuous and without any holes or perforations otherwise the dye vapour is able to penetrate to the substrate through the holes or perforations and so to superimpose on the decorative design an image of the holes or perforations. It is also desirable that the plastic film is uniform in thickness, within the usual commercial tolerances, so that the density of the decorative design does not vary according to any varying thickness of the plastic film. Of course, the thickness of the plastic film may be deliberately varied if it is required to achieve a particular effect by so doing. A simple way of varying the thickness is to use more than one thickness of plastic film in certain areas of the decorative design. However, once the dye concentration has been fully established in the variable thickness film, the effect resulting from the variable thickness will disappear. For this reason, although it is highly desirable that the plastic film is of uniform thickness except where special effects may be required, it is not absolutely essential as long as it is accepted that more of the first few transfers may not be satisfactory. It is essential that the plastic film is chemically stable at the transfer temperature. This transfer temperature is dependent, of course, on the substrate employed and on the sublimable dyes used. A simple means of choosing a plastic film is to use a film composed of the same material as the substrate. In this way, temperature stability, thermal expansion and other compatibility problems are eliminated. In addition, at the conditions which are suitable for heat transfer printing a particular substrate, it is clear that the diffusion rate of the dye molecules in that substrate (and hence in a plastic film of the same material) is correct for the process of the invention to proceed satisfactorily. As well as chemical stability, it is necessary that the plastic film has suitable physical stability at the transfer temperature ie that it does not

melt, shrink or wrinkle after one or several transfers. This is often a matter of selecting a plastic film grade which has been suitably oriented and stabilised by the manufacturers. The choice can be made by consulting the manufacturers' technical literature on this aspect. If necessary, the lowest possible transfer temperature combined with an appropriately longer transfer time may be chosen for a particular substrate and plastic film combination to reduce or eliminate shrinkage and wrinkling. Alternatively, the plastic film may be clamped or glued or fixed in some other way to a rigid frame to keep it taut and free from shrinkage and wrinkling during the transfer process. Materials of which the plastic film may be composed include acrylic polymers, polyamides, polyesters, copolyesters, epoxy resins, vinyl resins, polycarbonates, polyolefins or combinations of these materials. Preferred plastic film materials are polyester and polyamide since these materials are well suited to transfer printing and are often used as substrates. Polyethylene terephthalate is particularly suitable as a plastic film material since it may be obtained in a range of thicknesses, it has an excellent affinity for many sublimable dye molecules and it has an excellent temperature stability.

Where the process of this invention is used for the multiple transfer printing of a decorative design by interposing a dye-impermeable design carried on the plastic film between the transfer sheet and the substrate, it is necessary that the impermeable design is formed in some material which is totally 'opaque' to the sublimable dye. This generally means that it has no affinity for the dye. Suitable materials are metallic foils such as aluminium or copper foil or dye impermeable plastics such as polyimides. The impermeable material must be chemically and physically stable at the transfer temperature ie it must not shrink or melt, etc. It is preferable, although not essential, that the impermeable design be fixed to the plastic film in some way, such as by adhesion with a suitable temperature stable adhesive such as an epoxy or silicone adhesive, etc. If the design is not fixed to the plastic film, it is essential to locate the decorative design in exactly the same place in relation to the plastic film at each transfer otherwise the dye concentration gradient cannot be established correctly in the plastic film and 'ghost' images of the decorative design will be obtained as well as the desired imprint of the design. A convenient way of forming a decorative design which is attached to the plastic film is to use plastic film having a vapour deposited metallic layer and photo-etching away unwanted parts of the metallic layer. If necessary, the metallic layer may be electroplated before or after photo-etching in order to ensure that it is dye impermeable. Preformed metallic laminates with plastic film may also be used in the same way with the photo-etching technique. In general, it does not matter which surface of the plastic film is used to carry the decorative design. However, if the most accurate definition of the decorative design is required, it is preferable that it is carried on the side of the plastic film which is to be in contact with the substrate. In this case, it is necessary that the design formed from the impermeable material is a mirror image of the

decorative design which it is required to transfer print on to the substrate. If the decorative design formed from the impermeable material is carried between the transfer sheet and the plastic film, then it must be a right way round image of the decorative design. In some cases (for example, if the decorative design is composed of adhered metallic foil elements), it is easier to assemble the elements the right way round on the surface of the plastic film which will be in contact with the transfer sheet.

The following examples will serve to illustrate the invention. The examples are illustrated by Figures 1 to 3 and in these figures, items are labelled 'A' to 'E'. Item A is the transfer sheet with sublimable dye indicated by hatching on the surface of the sheet. Transfer sheet A has a uniform coating of sublimable dye of a single colour. Item B is the plastic film of this invention. Item C is the decorative design formed from dye-impermeable material, usually adhered to the plastic film with an adhesive layer which is not shown in the figures. Item D is the substrate on which the decorative design is to be printed by the heat transfer printing process. Item E is a second transfer sheet on which is imposed a multi-colour pattern in sublimable dyes; the different angles of hatching indicated the different sublimable dye colours.

#### Example 1 (illustrating multiple transfer printing)

In this example, A was a transfer sheet prepared by screen printing a uniform thin layer of MarlerTex TX01 screen printing ink containing a combination of sublimable dyes which give a black colour by transfer printing on to a coated art paper known as Marler Transfer Paper C17. Both the ink and the paper were supplied by E T Marler Ltd. The ink was printed and dried according to the instructions supplied by the manufacturers. Item B was clear Melinex Type 442 polyethylene terephthalate film manufactured by ICI and its thickness was 23 $\mu$ . Item C was a cutout shape in 20 $\mu$  thick aluminium foil. This foil was adhered to the face of the plastic film B which was to be in contact with the substrate D by the use of Scotch Spray Mount adhesive (manufactured by 3M United Kingdom Ltd). Item D was an off-white pigmented polyethylene terephthalate plastic sheet, Melinex Type 226 thickness 250 $\mu$  manufactured by ICI. These items were sandwiched together in the order shown in Figure 1 (ie ABCD) in a heat transfer press (A Adkins Model Double A Series 6000) with the transfer sheet A on top (ie immediately next to the heated surface of the press). The sandwich was then heated for 45 seconds at a temperature of 190°C under the pressure normally applied by this press. At the end of this time, the sandwich was removed from the press and the items (except B and C) were separated. Item A (the transfer sheet) was discarded. It was then observed that plastic film B was coloured black and that substrate D was uniformly light grey in colour except in the area which had been under the cutout aluminium foil design. The area which had been under the cutout foil design was not coloured by the sublimable dye contained on the transfer sheet. The definition of the edges of the design was extremely sharp and there were no speckles or other marks in any of the design areas reserved by the cutout foil design. No shading of the coloured areas attributable to structure in the plastic

film B could be detected. Items A and D were then replaced by unused pieces of transfer sheet and substrate respectively and the transfer printing process was repeated exactly as before using the original items B and C. This time, on examining substrate D, it was observed that the cutout foil design was reserved on a uniform dark grey background. Again, the edges of the design were sharply defined and no speckles or other marks were observed in the reserved areas which had been under the foil cutout nor was any structure which could have arisen from the plastic film B detectable in the dark grey areas. The printing procedure was then repeated once more with new pieces of transfer sheet A and substrate D. This time the cutout foil design was fully reserved on a very dark grey background with excellent edge definition and again no detectable structure superposition from the plastic film B. After carrying out the same transfer printing procedure for the fourth time, again under the same conditions as those used in the first printing, the fully reserved design was present on a black background. The edge definition remained excellent and no structure was detectable which could have arisen from the plastic carrier film B. A further sixteen printings were carried out in the same way as the first four and each one gave a reserved image on a black background. A very slight wrinkling of the plastic film B which had developed at the second printing did not reduce or get any more pronounced by the twentieth printing and it was concluded that virtually any number of heat transfer printings could be carried out if desired using the same plastic film B and cutout foil design C which was adhered to it. For comparison purposes, a sample of transfer sheet A was heat transfer printed in direct contact with a piece of substrate D for 45 seconds at 190°C. The substrate was coloured black and this colour was indistinguishable from that in the coloured areas of the substrate in the above replicate transfer printings 4 to 20.

#### Example 2 (comparative example)

Example 1 was repeated exactly but item B was in this case Kapton polyimide film Type 30H of 7.5 $\mu$  thickness manufactured by E I du Pont de Nemours & Co Inc in the USA. In this experiment, even after twenty attempted transfer printing operations, no colour was observed on the substrate D and the plastic film B (ie the Kapton film) was not coloured by the sublimable dye. It was also apparent that sublimable dye was not being removed from the transfer sheets A because after a successful transfer, the depth of colour on the transfer sheet is reduced and this is an obvious indication that sublimable dye is being transferred from the transfer sheet.

#### Example 3 (contamination prevention)

In this example (to which Figure 2 is applicable), item A, the transfer sheet, was an electrophotographically prepared transfer sheet on which a design was imprinted in mirror image form in a suitable medium containing a sublimable dye combination which gave a black colour when transfer printed on to a plastic or fabric substrate. The machinery and materials for preparing such electrophotographic transfer sheets are manufactured and sold by Subligraphic SA of Switzerland. In order for the electrophotographic process to work satisfactorily, the base material on

which the sublimable dye is deposited is a heavily coated electrostatic copying paper. Item B was Hostaphan polyethylene terephthalate film Type RE of thickness 2 $\mu$  manufactured by Hoechst AG of West Germany. Item D was a polyester coated copper satin steel plate (15 gauge) supplied by Charterhouse Xpres Ltd of the United Kingdom. These items were sandwiched together in the order shown in Figure 2 (ie ABD) and were placed in the heat transfer press described in Example 1. The plastic film B was in contact with the polyester coated face of the polyester coated copper satin steel plate. In this example, the sandwich was placed with the transfer sheet A at the bottom ie the back (non-coated) surface of the copper satin steel plate was immediately next to the heated surface of the press. The reason for this was that the high heat capacity of the copper satin steel would have led to a longer heating time if the heat had to be conducted through A and B. The sandwich was then heated for 45 seconds at a temperature of 190°C under the pressure normally applied by the press. At the end of this time, the sandwich was removed and transfer sheet A was discarded. A right way round image of the design was present on plastic film B. When plastic film B was peeled away from the polyester coating on the copper satin steel plate, this same image was present at full depth of colour on the polyester coating of the copper satin steel plate. The image was clear and distinct and there was no contamination of any kind on the surface of the polyester coating.

#### Example 4 (comparative example)

Example 3 was repeated exactly except that the plastic film B was omitted from the sandwich. After the heat transfer process, it was observed that the design on the transfer sheet was imprinted (the right way round) on the polyester coated copper satin steel plate. However, the surface of the polyester coating had on it a heavy white deposit which partly obscured the imprint of the design. This white deposit was believed to be a component of the coating on the base material of the transfer sheet. The white deposit could only be removed by vigorous rubbing with a cotton

swab soaked in ethyl alcohol.

Example 5 (illustrating multi-colour, multiple transfer printing)

Figure 3 is applicable to this example. The transfer sheet E was screen printed with a pattern which consisted of alternate touching bands of ink containing yellow and black sublimable dye respectively, each band being 10mm wide. All of the materials used in the preparation of this transfer sheet were as in Example 1 with the addition that the ink used for screen printing the bands containing the yellow dye was MarlerTex TX04. Items B, C and D were exactly as in Example 1 and the heat transfer process was carried out exactly as in Example 1 except that for each transfer process, the coloured bands of transfer sheet E were carefully placed in register with those which became imprinted on plastic film B. After four transfers, there was observed on substrate D a fully reserved design of the foil cutout C with a background of full depth colour bands of alternate yellow and black.

Example 6 (illustrating alternative position of the impermeable design)

Example 1 was repeated exactly except that the cutout foil design C was positioned between transfer sheet A and plastic film B. The results were the same as observed in Example 1 except that under microscopic examination (at 70x magnification) the edges of the reserved design on substrate D appeared slightly less well defined than those observed in Example 1. However, this difference was not apparent to the naked eye.

Examples 7 - 12 (showing the effect of plastic film thickness)

Example 1 was repeated but plastic film B was replaced by the plastic films noted in the table below. All other parameters, materials and operations were as in Example 1.

Table 1. The effect of the thickness of the plastic film B on the process of this invention. Transfer time 45 seconds. Temperature 190°C.

Example	Film Type	Thickness	Number of Transfers to Full Colour
7	Type RE	2 $\mu$	1
8	Type RE	6 $\mu$	1-2
9	Type RP	12 $\mu$	2-3
10	Type MN	19 $\mu$	3-4
11	Maylar D23	23 $\mu$	4-5
12	Maylar EB11	50 $\mu$	16

(Hostaphan is manufactured by Hoechst AG: Mylar is manufactured by E I du Pont de Nemours & Co Inc.)

#### Example 13 (textile substrate)

Example 1 was repeated but in place of Melinex plastic sheet, the substrate, item D, was a warp-knitted polyester fabric. In every transfer after the third, a reserved image of the foil cutout against a full depth black background was observed on the fabric.

#### CLAIMS

1. A process of heat transfer printing in which sublimable dye is transferred to a receiving substrate by molecular diffusion through a removable plastic film having an affinity for the sublimable dye.
2. A process as in 1. above where the plastic film is

composed substantially of polyester, copolyester, polyamide, polycarbonate, acrylic, PVC, polypropylene or any combination of these materials.

3. A process as in 1. above where the plastic film is composed substantially of polyester, copolyester or polyamide.

4. A process as in 1. above where the plastic film is composed substantially of polyethylene terephthalate, nylon 6 or nylon 6:6.

5. A process as in 1. above where the plastic film is composed substantially of polyethylene terephthalate.

6. A process as in 1. above where the plastic film is composed substantially of nylon 6:6.

7. A process as in 1. to 6. above where the plastic film is between  $2\mu$  and  $50\mu$  thick.
8. A process as in 1. to 6. above where the plastic film is between  $2\mu$  and  $25\mu$  thick.
- 5 9. A process as in 1. to 6. above where the plastic film is between  $2\mu$  and  $10\mu$  thick.
- 10 10. A process as in 1. to 6. above where the plastic film is between  $2\mu$  and  $6\mu$  thick.
11. A process as in 1. to 10. above where the receiving substrate is composed wholly or partially of thermoplastic fibres or films.
12. A process as in 1. to 10. above where the receiving substrate is composed wholly or partially of polyester, copolyester or polyamide.
- 15 13. A process as in 1. to 10. above where the receiving substrate is composed wholly or partially of polyethylene terephthalate, nylon 6 or nylon 6:6.
14. A process as in 1. to 10. above where the receiving substrate is composed wholly or partially of polyethylene terephthalate or a copolymer of polyethylene terephthalate.
- 20 15. A process as in 1. to 10. above where the receiving substrate is composed wholly or partially of polyethylene terephthalate.
- 25 16. A process as in 1. to 10. above where the receiving substrate comprises a plastic coating on a support, the plastic coating being composed substantially of polyethylene terephthalate or a copolymer of polyethylene terephthalate.
- 30 17. Heat transfer prints produced by the process as claimed in claims 1. to 16. above.

